Supporting Information:

Stress in a stimuli-responsive polymer brush

M. Manav,*† M. Ponga,*† and A. Srikantha Phani,*‡

†Graduate Aerospace Laboratories, California Institute of Technology, Pasadena, USA
‡Mechanical Engineering, University of British Columbia, Vancouver, Canada

E-mail: manav@alumni.ubc.ca; mponga@mech.ubc.ca; srikanth@mech.ubc.ca

S1 SST formulation

Elongation of a freely jointed chain due to an end stretching force $p$ is a function of $p$ and is defined as:

$$e(p) = \frac{z}{Na}, \quad (S1)$$

where $z$ is end to end distance, and $Na$ is contour length of a chain. For a chain in a nonuniform field, elongation needs to be defined locally as stretching force changes along the length of the chain. In this case,

$$e(p) = \frac{1}{n} \frac{dz}{dn}, \quad (S2)$$

where $dn$ monomers of a chain are contained in a thin layer of thickness $dz$ at height $z$ as shown in Figure 1. $p$ is local elongation force and the static equilibrium of $n$–th segment of the chain yields the following relation between the potential field and stretching force:¹

$$\frac{dp}{dn} = \frac{dp}{dz} \frac{dz}{dn} = -\frac{\partial V(z)}{\partial z}. \quad (S3)$$
By combining (S2) and (S3), relation between local elongation force in a chain segment at height $z$ and the potential field is obtained.

$$E(p) = a \int_{0}^{p} e(p') dp' = V(z_e) - V(z), \quad (S4)$$

where $z_e$ is location of the chain end. $E(p)$ is the complementary stretching energy stored in a portion of a chain of length of a monomer and this function depends on the model of ideal chain. This work uses ideal chain model with force-extension relation given by Langevin function to account for finite extensibility of a polymer chain. Also, the above equation suggest that the stretching force in a chain at height $z$ depends on the location of the chain end $z_e$.

In our monodisperse polymer chain, each chain has $N$ monomers. Hence, $\int_{0}^{N} dn = N$. Using (S2), this relation can be expressed as:

$$\int_{0}^{N} dn = \int_{0}^{z_e} \frac{dz}{ae(p)} = N. \quad (S5)$$

Notice that using (S4), $p = E^{-1}(V(z_e) - V(z))$, where $E^{-1}$ is inverse function of $E$. Hence, $e(p) = \Lambda(V(z_e) - V(z))$, where $\Lambda(\cdot) = e(E^{-1}(\cdot))$. The constraint in (S5) can then be expressed as follows:

$$\int_{0}^{z_e} \frac{dz}{N a \Lambda(V(z_e) - V(z))} = 1. \quad (S6)$$

The above integral equation can be solved to obtain $V(z)$ once an appropriate model of a polymer chain, that is the form of $e(p)$, for the given polymer is ascertained.

Now, let $g(z)$ define the density of chain ends within the brush. Then, the self consistency requirement necessitates the following relation between polymer volume fraction ($\phi(z)$), end density and the potential field:

$$\phi(z) = \int_{z}^{H} v_0 \left( \frac{dn}{dz}(z, z_e) \right) g(z_e) dz_e = v_0 \int_{z}^{H} \frac{g(z_e)}{a \Lambda(V(z_e) - V(z))} dz_e, \quad (S7)$$
Once $V(z)$ is determined by solving the integral equation (S6), $\phi(z)$ can be obtained by solving (5). The above integral equation can then be solved to obtain end density $g(z)$ in a brush.

On using the nondimensionalization scheme given in Appendix A, Eqs. (S4), (S6), and (S7) turn into (3), (4), and (6), respectively in the main text.

### S2 End density distribution

At first, polymer volume fraction $\phi(z)$ for a brush is calculated using (5). Then for known $\phi(z)$, the integral equation (6) needs to be solved to find end density distribution. Following the approach employed by Amoskov et al.,\(^1\) we use the method of Laplace transform to solve the equation.

Starting with (4), let us assume $u = \bar{V}(\bar{z}_e)$ and $v = \bar{V}(\bar{z})$. Using a change in variable, (4) can be written as:

$$\int_0^u d\bar{z} \frac{dv}{dv} \Lambda(u - v) = 1.$$  \hfill (S8)

On using Laplace transform for convolution of two functions, the above transforms to:

$$\mathcal{L}\left(\frac{d\bar{z}_e}{du}\right) \mathcal{L}\left(\frac{1}{\Lambda(u)}\right) = \frac{1}{s}.$$  \hfill (S9)

Then the potential field $u$ can be found by wring the above as

$$\mathcal{L}\left(\frac{d\bar{z}_e}{du}\right) = \frac{1}{s} \left(\mathcal{L}\left(\frac{1}{\Lambda(u)}\right)\right)^{-1}.$$  \hfill (S10)

and obtaining inverse Laplace transform. For a Langevin chain, a series solution for $\bar{V}(\bar{z})$ was obtained\(^1\) using the above and a Padé approximation of the series solution was also reported.\(^2\)

Depending on $\bar{\phi}(\bar{z})$ profile, we may have distinct cases to solve to obtain end density profile. Here, we consider two cases. In the first case, there are no discontinuities in the
polymer volume fraction profile inside the brush, though it can have a discontinuity at the brush free end. In the second case, the brush has a discontinuity in the polymer volume fraction profile inside the brush. Below, we first obtain the expression for end distribution $\bar{g} (\bar{z})$ for the first case, followed by the second case.

S2.1 No jump in the volume fraction profile inside the brush

Let us assume $\bar{u} = \bar{V}(\bar{H}) - \bar{V}(\bar{z})$ and $\bar{v} = \bar{V}(\bar{H}) - \bar{V} (\bar{z}_e)$. Then (6) transforms to the following:

$$R (\bar{u}) = \int_0^{\bar{u}} \frac{q (\bar{v})}{\bar{N} (\bar{u} - \bar{v})} d \bar{v}, \quad q (\bar{v}) = -\bar{g} (\bar{z}_e) \frac{d \bar{z}_e}{d \bar{v}}, \quad R (\bar{u}) = \bar{\phi} (\bar{z}). \quad (S11)$$

By taking the Laplace transform of the above, we obtain:

$$\mathcal{L} (R (\bar{u})) = \mathcal{L} (q (\bar{u})). \mathcal{L} \left( \frac{1}{\bar{N} (\bar{u})} \right). \quad (S12)$$

Using (S9) in the above, we obtain:

$$\mathcal{L} (q (\bar{u})) = s \mathcal{L} (R (\bar{u})). \mathcal{L} \left( \frac{d \bar{z}_f}{d \bar{u}} \right)$$

$$= \left( \mathcal{L} \left( \frac{d R (\bar{u})}{d \bar{u}} \right) + R (0) \right). \mathcal{L} \left( \frac{d \bar{z}_f}{d \bar{u}} \right), \quad (S13)$$

where $\bar{u} = \bar{V} (\bar{H}) - \bar{V} (\bar{z}) = \bar{V} (\bar{z}_f)$. By taking inverse Laplace transform of the above equation, we obtain:

$$q (\bar{u}) = \int_0^{\bar{u}} \frac{d \bar{z}_f'}{d \bar{v}} \frac{d R (\bar{\hat{v}})}{d \bar{\hat{v}}} d \bar{\hat{v}} + R (0) \frac{d \bar{z}_f}{d \bar{u}}, \quad (S14)$$

where $\bar{\hat{v}} = \bar{u} - \bar{v}$ and $\bar{v} = \bar{V} (\bar{H}) - \bar{V} (\bar{z}_e) = \bar{V} (\bar{z}_f')$. Then using (S11), we obtain the expression for end density.

$$\bar{g} (\bar{z}) = \frac{d V (\bar{z})}{d \bar{z}} \left( \int_0^{\bar{z}_f} \frac{d R (\bar{\hat{v}})}{d \bar{\hat{v}}} d \bar{\hat{v}}' + R (0) \frac{d \bar{z}_f}{d \bar{u}} \right). \quad (S15)$$

As $R (0) = \bar{\phi} (\bar{H})$, the last term contributes only when the volume fraction profile has a jump at the brush free end. Also, as $\bar{z} \to \bar{H}, \bar{z}_f \to 0$ and $\frac{d \bar{u}}{d \bar{z}_f} \to 0$. Thus, end density diverges and
has a vertical asymptote at \( \bar{z} = \bar{H} \) when \( \bar{\phi}(\bar{H}) \neq 0 \), as observed in a collapsed brush.

To calculate \( \frac{dR(\hat{v})}{\hat{v}} \), we write \( \hat{v} = \bar{u} - \bar{v} = \bar{V}(\bar{H}) - \bar{V}(\bar{z}) - \bar{V}(\bar{z}_f') = \bar{V}(\bar{H}) - \bar{V}(\bar{z}_f') \), where \( \bar{V}(\bar{z}) + \bar{V}(\bar{z}_f') = \bar{V}(\bar{z}_f^*) \). Also, \( R(\hat{v}) = \bar{\phi}(\bar{z}_f^*) \) using (S11). Then,

\[
\frac{dR(\hat{v})}{d\hat{v}} = \frac{d\bar{\phi}(\bar{z}_f^*)}{d\hat{v}} = -\frac{d\bar{\phi}(\bar{z}_f^*)}{d\bar{V}(\bar{z}_f')}, \tag{S16}
\]

where \( \bar{\phi}(\bar{z}_f^*) \) is obtained by using (5) as follows:

\[
\bar{V}(\bar{H}) - \bar{V}(\bar{z}_f^*) = \bar{V}(\bar{H}) - \bar{V}(\bar{z}) - \bar{V}(\bar{z}_f') = \mu(\bar{\phi}(\bar{z}_f^*)) - \bar{\mu}(\bar{\phi}(\bar{H})). \tag{S17}
\]

Furthermore, differentiation of the above equation yields:

\[
-\frac{d\bar{V}(\bar{z}_f^*)}{d\bar{\phi}(\bar{z}_f^*)} = \frac{d\bar{\mu}(\bar{\phi}(\bar{z}_f^*))}{d\bar{\phi}(\bar{z}_f^*)} \tag{S18}
\]

Since \( \frac{d\bar{\phi}(\bar{z}_f^*)}{d\bar{V}(\bar{z}_f^*)} = \left(\frac{d\bar{V}(\bar{z}_f^*)}{d\bar{\phi}(\bar{z}_f^*)}\right)^{-1} \), and \( \bar{\mu}(\bar{\phi}) \) and consequently its derivative are known for the polymer, the above equation allows evaluation of (S16).

### S2.2 Jump in the volume fraction profile inside the brush

If the polymer volume fraction profile has a jump at the height \( \bar{z} = \bar{H}_t \) inside the brush, then (S11) needs to be divided into the two following cases:

\[
R(\bar{u}) = \begin{cases} 
\int_{\bar{u}}^{\bar{u}_t} \frac{q(v)}{\Lambda(\bar{u} - v)} d\bar{v}, & \bar{u} < \bar{u}_t \\
\int_{\bar{u}}^{\bar{u}_t} \frac{q(v)}{\Lambda(\bar{u} - v)} d\bar{v} + v_0 \int_{\bar{u}_t}^{\bar{u}_t + \epsilon} \frac{q(v)}{\Lambda(\bar{u} - v)} d\bar{v}, & \bar{u} > \bar{u}_t 
\end{cases} \tag{S19}
\]

where \( \bar{u}|_{z=\bar{H}_t} = \bar{u}_t \), and \( \bar{u}_t^- = \bar{u}_t - \epsilon \) and \( \bar{u}_t^+ = \bar{u}_t + \epsilon \), \( \epsilon \to 0 \). In the first case, that is when \( \bar{H}_t < \bar{z} < \bar{H} \), end density is given by (S15). In this section, we obtain the end density for the second case, that is \( \bar{z} < \bar{H}_t \).

In the second case, the first integral in the expression can be calculated by using the
result from the first case. Then the equation can be transformed into the following form:

\[
S(\bar{u}) = \int_{0}^{\bar{u}} \frac{\bar{q}(\bar{v})}{\Lambda(\bar{u} - \bar{v})} d\bar{v},
\]

where,

\[
S(\bar{u}) = R(\bar{u}) - \int_{0}^{\bar{u}-} \frac{q(\bar{v}_{h})}{\Lambda(\bar{u} - \bar{v}_{h})} d\bar{v}_{h} = R(\bar{u} + \alpha) - \int_{0}^{\bar{u}-} \frac{q(\bar{v}_{h})}{\Lambda(\bar{u} + \alpha - \bar{v}_{h})} d\bar{v}_{h},
\]

and \(\bar{u} = \bar{V}(\bar{H}_{t}) - \bar{V}(\bar{z}) = \bar{u} - \alpha, \alpha = \bar{V}(\bar{H}) - \bar{V}(\bar{H}_{t}), \bar{v} = \bar{V}(\bar{H}_{t}) - \bar{V}(\bar{z}_{g}), \bar{v}_{h} = \bar{V}(\bar{H}) - \bar{V}(\bar{z}_{h}), q(\bar{v})d\bar{v} = \bar{q}(\bar{v})d\bar{v} = -\bar{g}(\bar{z}_{e})d\bar{z}_{e},\) and we have replaced the integration variable \(\bar{v}\) with \(\bar{v}_{h}\). Note that (S20) has the same form as (S11). So, following the same procedure as employed in solving (S11), we obtain:

\[
\bar{q}(\bar{u}) = \int_{0}^{\bar{u}} \frac{d\bar{z}_{g}'}{d\bar{v}} dS(\bar{v}) \frac{d\bar{z}_{g}}{d\bar{u}} + S(0) \frac{d\bar{z}_{g}}{d\bar{u}},
\]

where \(\bar{v} = \bar{u} - \bar{v}, \) and \(\bar{u} = \bar{V}(\bar{H}_{t}) - \bar{V}(\bar{z}) = \bar{V}(\bar{z}_{g})\) and \(\bar{v} = \bar{V}(\bar{H}_{t}) - \bar{V}(\bar{z}_{e}) = \bar{V}(\bar{z}_{g}').\) Then using the relation \(\bar{g}(\bar{z}) = -\bar{q}(\bar{u}) \frac{d\bar{u}}{d\bar{z}}\), we obtain the expression for \(\bar{g}(\bar{z}).\)

\[
\bar{g}(\bar{z}) = \frac{d\bar{V}(\bar{z})}{d\bar{z}} \left( \int_{0}^{\bar{z}_{g}} \frac{dS(\bar{v})}{d\bar{v}} d\bar{z}_{g}' + S(0) \frac{d\bar{z}_{g}}{d\bar{u}} \right).
\]

Note that \(\bar{u} = 0,\) when \(\bar{z} = \bar{H}_{t}.\) Hence, \(S(0) = \bar{\phi}(\bar{H}_{t}-) - \bar{\phi}(\bar{H}_{t}+),\) that is, it equals the jump in the polymer volume fraction at \(\bar{z} = \bar{H}_{t}.\) Also, since \(\bar{z}_{g} \rightarrow 0\) and \(\frac{d\bar{v}}{d\bar{z}_{g}} \rightarrow 0\) when \(\bar{z} \rightarrow \bar{H}_{t},\) end density diverges and has a vertical asymptote at \(\bar{z} = \bar{H}_{t}\) within the brush.

To be able to calculate \(\bar{g}(\bar{z}),\) we first need to determine \(\frac{dS(\bar{v})}{d\bar{v}}.\) By replacing \(\bar{u}\) with \(\bar{v}\) in
(S21), and taking derivative, we get:

\[
\frac{dS(\hat{v})}{d\hat{v}} = \frac{dR(\hat{v} + \alpha)}{d\hat{v}} + \int_{\hat{v}_h}^{\hat{v}} \frac{q(\hat{v}_h)}{(\Lambda(\hat{v} + \alpha - \hat{v}_h))^2} \frac{d\bar{\Lambda}(\hat{v} + \alpha - \hat{v}_h)}{d\hat{v}} d\hat{v}_h
\]

\[
= \frac{dR(\hat{v} + \alpha)}{d\hat{v}} + \int_{\hat{v}_h}^{\bar{H}} \frac{\bar{g}(\hat{v}_h) d\bar{z}_h}{(\Lambda(\hat{v} + \alpha - \hat{v}_h))^2} \frac{d\bar{\Lambda}(\hat{v} + \alpha - \hat{v}_h)}{d\hat{v}}.
\]

To calculate \(\frac{dR(\hat{v} + \alpha)}{d\hat{v}}\), we write \(\hat{v} + \alpha = \bar{V}(\bar{H}) - \bar{V}(\bar{z}) - \bar{V}(\bar{z}'_g) = \bar{V}(\bar{H}) - \bar{V}(\bar{z}_g^*)\), where \(\bar{V}(\bar{z}) + \bar{V}(\bar{z}'_g) = \bar{V}(\bar{z}_g^*)\). Then \(R(\hat{v} + \alpha) = \bar{\phi}(\bar{z}_g^*)\). Also,

\[
\frac{dR(\hat{v} + \alpha)}{d\hat{v}} = \frac{d\bar{\phi}(\bar{z}_g^*)}{d\hat{v}} = -\frac{d\bar{\phi}(\bar{z}_g^*)}{d\bar{V}(\bar{z}_g^*)}.
\]

\(\bar{\phi}(\bar{z}_g^*)\) is obtained by solving the following equation obtained by using (5).

\[
\bar{V}(\bar{H}) - \bar{V}(\bar{z}_g^*) = \bar{V}(\bar{H}) - \bar{V}(\bar{z}) - \bar{V}(\bar{z}_g^*) = \bar{\mu}(\bar{\phi}(\bar{z}_g^*)) - \bar{\mu}(\bar{\phi}(\bar{H})).
\]

Afterwards differentiation of the above relation gives:

\[
-\frac{d\bar{V}(\bar{z}_g^*)}{d\bar{\phi}(\bar{z}_g^*)} = \frac{d\bar{\mu}(\bar{\phi}(\bar{z}_g^*))}{d\bar{\phi}(\bar{z}_g^*)}.
\]

As \(\frac{d\bar{\phi}(\bar{z}_g^*)}{d\bar{V}(\bar{z}_g^*)} = \left(\frac{d\bar{V}(\bar{z}_g^*)}{d\bar{\phi}(\bar{z}_g^*)}\right)^{-1}, \frac{dR(\hat{v} + \alpha)}{d\hat{v}}\) can be calculated.

Evaluation of the term with integral in (S24) requires us to first calculate \(\frac{d\bar{\Lambda}(\hat{v} + \alpha - \hat{v}_h)}{d\hat{v}}\) which can be simplified to the following form:

\[
\frac{d\bar{\Lambda}(\hat{v} + \alpha - \hat{v}_h)}{d\hat{v}} = -\frac{d\bar{\Lambda}(\bar{V}(\bar{z}_h) - \bar{V}(\bar{z}_g^*))}{d\bar{V}(\bar{z}_g^*)}.
\]

Remember that \(\bar{\Lambda}(\bar{V}(\bar{z}_h) - \bar{V}(\bar{z}_g^*)) = \bar{e}(\bar{p}_g^*),\) where \(\bar{p}_g^*\) is the local stretching force at height \(\bar{z}_g^*\) in a polymer chain with end at \(\bar{z}_h,\) and \(\bar{e}(\bar{p}_g^*)\) is local stretching in a chain due to the stretching
force \( \tilde{p}_g^* \). Also, from (3), \( \bar{E}(\tilde{p}_g^*) = \bar{V}(\tilde{z}_h) - \bar{V}(\tilde{z}_g^*) \). Taking derivative of this expression gives:

\[
\frac{1}{r_k} \bar{e}(\tilde{p}_g^*) \frac{d\tilde{p}_g^*}{d\bar{V}(\tilde{z}_g^*)} = -1,
\]

where we have used \( \frac{d\bar{E}(\tilde{p}_g^*)}{d\tilde{p}_g^*} = \frac{\bar{e}(\tilde{p}_g^*)}{r_k} \) following (3). Then substituting the above result in (S28) yields:

\[
\frac{d\bar{\Lambda}(\tilde{\nu} + \alpha - \tilde{v}_h)}{d\tilde{\nu}} = - \frac{d\bar{\Lambda}(\bar{V}(\tilde{z}_h) - \bar{V}(\tilde{z}_g^*)))}{d\bar{V}(\tilde{z}_g^*)} = - \frac{d\bar{e}(\tilde{p}_g^*)}{d\tilde{p}_g^*} \frac{d\tilde{p}_g^*}{d\bar{V}(\tilde{z}_g^*)} = \frac{r_k}{\bar{e}(\tilde{p}_g^*)} \frac{d\bar{e}(\tilde{p}_g^*)}{d\tilde{p}_g^*} \frac{d\tilde{p}_g^*}{d\bar{V}(\tilde{z}_g^*)}.
\]

S3 Stress calculation

In this section, the stress calculation in the regions with continuous volume fraction profile is described first, followed by the calculation of the stress at the interface.

S3.1 In the regions with continuous volume fraction

Evaluating stress requires us to first calculate the derivative terms \( \frac{\partial \varepsilon_{xz}(z)}{\partial \varepsilon_{xx}} \) and \( \frac{\partial f(z)}{\partial \varepsilon_{xx}} \) in (18). We start by calculating \( \frac{\partial \varepsilon_{xz}(z)}{\partial \varepsilon_{xx}} \), which can be written as:

\[
\frac{\partial \varepsilon_{xz}}{\partial \varepsilon_{xx}} = \frac{\partial}{\partial \varepsilon_{xx}} \left( \frac{\partial \tilde{u}_z}{\partial \tilde{z}} \right) = \frac{\partial}{\partial \tilde{z}} \left( \frac{\partial \tilde{u}_z}{\partial \varepsilon_{xx}} \right),
\]

where \( \tilde{u}_z = u_z/(Na) \) is the nondimensionalized displacement of a thin layer at \( z \) shown in Figure 1 in the \( z \)-direction due to the applied strain \( \varepsilon_{xx} \). In order to evaluate \( \frac{\partial \tilde{u}_z}{\partial \varepsilon_{xx}} \) and subsequently \( \frac{\partial \varepsilon_{xz}}{\partial \varepsilon_{xx}} \), we enforce the condition that a thin layer within the brush as shown in Figure 1 is defined by the monomers (total number \( V_0 \tilde{\phi}/v_0 \), where \( V_0 \) is initial layer volume) inside it, and on applying a strain, no monomer moves in or out of the layer. Hence, \( \Delta(V_0 \tilde{\phi}/v_0) = 0 \), which on simplification yields\(^3\):

\[
\frac{\partial}{\partial \tilde{z}} \left( \frac{\partial \tilde{u}_z}{\partial \varepsilon_{xx}} \right) = - \frac{1}{\tilde{\phi}} \frac{\partial \tilde{\phi}}{\partial \varepsilon_{xx}} - 1,
\]
with the boundary condition in the case of no vertical phase separation within a brush as given below:

\[
\left[ \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \right]_{\bar{z} = \bar{H}} = \frac{\partial \bar{H}}{\partial \epsilon_{xx}}. \quad \text{(S33)}
\]

We obtain \( \frac{\partial \bar{\phi}}{\partial \epsilon_{xx}} \) by taking derivative of the (5) and simplifying the resulting expression.

\[
\frac{\partial \bar{\phi}}{\partial \epsilon_{xx}} = \left( d\bar{V}(\bar{H}) \frac{\partial \bar{H}}{\partial \epsilon_{xx}} - d\bar{V}(\bar{z}) \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \right) \frac{d\bar{\mu}(\bar{\phi})}{d\bar{\phi}}, \quad \text{(S34)}
\]

where \( \frac{\partial \bar{H}}{\partial \epsilon_{xx}} = \frac{\partial \bar{H}}{\partial \rho_g} \frac{d\rho_g}{d\epsilon_{xx}} \) is obtained by numerically solving (5) for a range of graft densities and obtaining \( \frac{\partial \bar{H}}{\partial \rho_g} \). Since graft density after the strain \( \epsilon_{xx} \) is applied is \( \approx \rho_g(1 - \epsilon_{xx}) \), \( \frac{d\rho_g}{d\epsilon_{xx}} = -\rho_g \).

After that, by solving (S32) along with (S34) and the boundary condition in (S33), \( \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \) is obtained.

In the case of a vertical phase separation within a brush, domain is divided into two. For the inner domain, that is \( \bar{z} < \bar{H}_t \), boundary condition is as follows:

\[
\left[ \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \right]_{\bar{z} = 0} = 0. \quad \text{(S35)}
\]

For \( \bar{H}_t < \bar{z} \leq \bar{H} \), (S32) is solved with the following boundary condition:

\[
\left[ \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \right]_{\bar{z} = \bar{H}} = \frac{\partial \bar{H}}{\partial \epsilon_{xx}}. \quad \text{(S36)}
\]

It should be noted that this leads to a discontinuous \( \bar{u}_z(\bar{z}) \) and consequently discontinuous \( \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}} \). In a solid material, a discontinuous \( \bar{u}_z \) results from fracture. However, here a discontinuous \( \bar{u}_z \) indicates that in a layer very close to \( \bar{H}_t \), polymer volume fraction undergoes a sudden jump as a result of the applied strain \( \epsilon_{xx} \).

To calculate the derivative of free energy density, the derivative of the two contributions to the free energy density are calculated separately.

\[
\frac{\partial f(\bar{z})}{\partial \epsilon_{xx}} = \frac{\partial f_{\text{int}}(\bar{z})}{\partial \epsilon_{xx}} + \frac{\partial f_{\text{el}}(\bar{z})}{\partial \epsilon_{xx}}. \quad \text{(S37)}
\]
To calculate the first term, we recognize that

\[
\frac{\partial f_{int}(\bar{z})}{\partial \epsilon_{xx}} = \frac{k_B T}{v_0} \bar{\mu}(\bar{\phi}(\bar{z})) \frac{\partial \bar{\phi}(ar{z})}{\partial \epsilon_{xx}},
\] (S38)

and \(\frac{\partial \bar{\phi}(\bar{z})}{\partial \epsilon_{xx}}\) is obtained from (S34). To evaluate \(\frac{\partial f_{el}(\bar{z})}{\partial \epsilon_{xx}}\), we take derivative of (14), which yields:

\[
\frac{\partial f_{el}}{\partial \epsilon_{xx}} = \frac{k_B T}{v_0 r_k} \int_\bar{z}^H \log \left( \frac{\sinh(\bar{p})}{\bar{p}} \right) \left( 1 - \frac{\coth(\bar{p})^2 + 1}{\bar{p}^2} \right) \bar{g}(\bar{z}_e) \frac{\partial \bar{p}}{\partial \epsilon_{xx}} d\bar{z}_e
\]

\[
+ \frac{k_B T}{v_0 r_k} \int_\bar{z}^H \left( \bar{p} - \frac{1}{\bar{e}(\bar{p})} \log \left( \frac{\sinh(\bar{p})}{\bar{p}} \right) \right) \frac{\partial \bar{g}(\bar{z}_e)}{\partial \epsilon_{xx}} d\bar{z}_e,
\] (S39)

where

\[
\frac{\partial \bar{p}}{\partial \epsilon_{xx}} = -r_k \frac{\partial \bar{V}(\bar{z})}{\partial \epsilon_{xx}} = -\frac{1}{\bar{e}(\bar{p})} \frac{8}{5} \frac{2\bar{z}^2 + 4\bar{z}^2 + 5}{(1 - \bar{z}^2)^2} \frac{\partial \bar{u}_z}{\partial \epsilon_{xx}}.
\] (S40)

Since \(\bar{e}(\bar{p}) \to 0\) as \(\bar{p} \to 0\), \(\frac{\partial \bar{p}}{\partial \epsilon_{xx}} \to \infty\). Also, in the case of phase separation, \(\bar{g}(\bar{z}_e)\) diverges.

These lead to improper integrals in the expression for \(\frac{\partial f_{el}}{\partial \epsilon_{xx}}\) which require appropriate variable transformations in the expression for \(f_{el}\) in order to numerically calculate them.

### S3.2 At the interface

At the interface in a brush with vertical phase separation, \(\delta(f(\bar{z})V)\) in (16) equals the difference in the free energy contained in region 2 and region 1 (see Figure 2).

\[
f_2 A (1 + \delta \epsilon_{xx}) (\delta \bar{H}_t + [\delta \bar{u}_z]_{\bar{z} = \bar{H}_t} - [\delta \bar{u}_z]_{\bar{z} = \bar{H}_t - \delta \bar{H}_t}) - f_1 A \delta \bar{H}_t = \sigma_{xx} \delta \epsilon_{xx} A \delta \bar{H}_t,
\] (S41)

where \(A\) is substrate surface area, and \(\delta \bar{u}_z = \bar{u}_z/(Na)\) is the nondimensionalized displacement of the monomers at \(\bar{z}\) in the \(z\)-direction due to the applied strain \(\delta \epsilon_{xx}\). As mentioned in the main text, \(f_2\) and \(f_1\) are the free energy densities right above the interface \((\bar{H}_t + \delta, \delta \to 0)\) in the deformed brush and right below the interface \((\bar{H}_t - \delta, \delta \to 0)\) in the initial brush, respectively. \(\phi^+\) and \(\phi^-\) are the coexisting polymer volume fractions at the interface (see Figure 2). \(\delta \bar{H}_t\) is chosen such that on applying \(\delta \epsilon_{xx}\), the monomers at \(\bar{H}_t - \delta \bar{H}_t\) in the...
undeformed brush lie at the new interface in the deformed brush. On dividing by \((\delta \epsilon_{xx})^2\), (S41) simplifies to the following in the limit of \(\delta \epsilon_{xx} \rightarrow 0\):

\[
\frac{\sigma_{xx} \partial \tilde{H}_t}{\partial \epsilon_{xx}} = \lim_{\delta \epsilon_{xx} \rightarrow 0} \frac{f_2(1 + \delta \epsilon_{xx}) \left( \frac{\partial \tilde{H}_t}{\partial \epsilon_{xx}} + \left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t} - \left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t - \delta \tilde{H}_t} \right) - f_1 \frac{\partial \tilde{H}_t}{\partial \epsilon_{xx}}}{\delta \epsilon_{xx}}.
\]  

(S42)

In a brush with vertical phase separation, \(\frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}}\) is also discontinuous and \(\left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t} - \left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t - \delta \tilde{H}_t}\) equals the jump in the profile at \(\tilde{H}_t\) and is finite. To find \(\frac{\partial \tilde{H}_t}{\partial \epsilon_{xx}}\), we make use of mass conservation, that is the volume of the monomers contained in region 1 and region 2 in Figure 2 are equal.

\[
\phi^- A (1 + \delta \epsilon_{xx}) (\delta \tilde{H}_t + [\delta \tilde{u}_z]_{\tilde{z} = \tilde{H}_t} - [\delta \tilde{u}_z]_{\tilde{z} = \tilde{H}_t - \delta \tilde{H}_t}) - \phi^+ A \delta \tilde{H}_t = 0.
\]  

(S43)

On dividing the above equation by \(\delta \epsilon_{xx}\), taking the limit \(\delta \epsilon_{xx} \rightarrow 0\) and simplifying, we obtain

\[
\frac{\partial \tilde{H}_t}{\partial \epsilon_{xx}} = \phi^- \left( \left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t} - \left[ \frac{\partial \tilde{u}_z}{\partial \epsilon_{xx}} \right]_{\tilde{z} = \tilde{H}_t - \delta \tilde{H}_t} \right). 
\]  

(S44)

We substitute this in (S42) to obtain the expression for the stress at the interface.

\[
\sigma_{xx}(\tilde{H}_t) = \lim_{\delta \epsilon_{xx} \rightarrow 0} \frac{1}{\phi^-} \frac{f_2 \phi^+ - f_1 \phi^-}{\delta \epsilon_{xx}}.
\]  

(S45)

The free energy densities can be divided in their interaction and elastic components, which
can be written as follows using (13) and (14).

\[ f_{1\text{int}} = \left[ (1 - \phi^+) \log(1 - \phi^+) + \chi \phi^+(1 - \phi^+) \right] \frac{k_B T}{v_0}, \]

\[ f_{2\text{int}} = \left[ (1 - \phi^-) \log(1 - \phi^-) + \chi \phi^-(1 - \phi^-) \right] \frac{k_B T}{v_0}, \]

\[ f_{1\text{el}} = \frac{k_B T}{v_0} \int_{\bar{H}}^{\bar{H}_t} \frac{1}{r_k \bar{e}(\bar{p})} \left( \bar{p} \bar{e}(\bar{p}) - \log \left( \frac{\sinh(\bar{p})}{\bar{p}} \right) \right) \bar{g}(\bar{Z}_e) d\bar{Z}_e, \]

\[ f_{2\text{el}} = f_{1\text{el}} + \left[ \frac{\partial f_{\text{el}}(\bar{Z})}{\partial \epsilon_{xx}} \right]_{\bar{z} = \bar{H}_t} \delta \epsilon_{xx}, \]  
\text{(S46)}

where the expression for \( f_{2\text{el}} \) uses continuity of \( f_{\text{el}} \) even in case of a vertical phase separation.

Note that the discontinuity in volume fraction causes only a corner in elastic free energy density profile. \( f_{1\text{el}} \) and \( \left[ \frac{\partial f_{\text{el}}(\bar{Z})}{\partial \epsilon_{xx}} \right]_{\bar{z} = \bar{H}_t} \) have already been calculated in the previous section. Substituting (S46) in (S45) yields:

\[ \sigma_{xx}(\bar{H}_t) = \lim_{\delta \epsilon_{xx} \rightarrow 0} \frac{1}{\phi^-} \left( f_{2\text{int}}(\phi^+) - f_{1\text{int}}(\phi^-) \right) + f_{1\text{el}}(\phi^+ - \phi^-) + \frac{\phi^+}{\phi^-} \left[ \frac{\partial f_{\text{el}}(\bar{Z})}{\partial \epsilon_{xx}} \right]_{\bar{z} = \bar{H}_t}. \]  
\text{(S47)}

### S4 Brush height and the maximum volume fraction

Variation in brush height with graft density is also temperature dependent (\( \bar{H} \sim \rho_g^{n(T,\bar{\rho}_g)} \)) and shows a nonmonotonic behavior in a narrow temperature range as shown in Figure S1. At temperatures below 30 °C, \( n \approx 1/3 \) in the low graft density regime. At very high graft densities, \( n \) approaches 1, as expected for extremely dense brushes. In between these two limits, \( n \) exhibits atypical behavior and approaches 0 before recovering and approaching 1. At 33 °C and above, the height variation is close to \( \bar{\rho}_g \).

The maximum polymer volume fraction in a brush occurs near the grafting surface and is plotted as a function of graft density in Figure S1 at different temperatures. Like the volume fraction profile, it shows a discontinuity at temperatures between 26.36 °C and 30.5 °C. At temperatures above 30.5 °C, it shows minimal change with graft density for low graft density brushes.
Interestingly, dependence of brush height on graft density even in a good solvent condition diminishes \( n(T, \tilde{\rho}_g) < 1/3 \) as graft density increases, before picking up again above \( \tilde{\rho}_g \gtrsim 0.3 \). This engenders from mild change in interaction free energy density of PNIPAm between volume fractions \( \sim 0.4 \) and \( \sim 0.8 \) (see Figure 3). In the narrow range of graft density in which volume fraction in a large section of a brush is in this range, on increasing graft density, brush accommodates extra monomers closer to grafting surface, incurring small interaction energy penalty to achieve only a small increase in stretching energy in the brush. For temperatures at which vertical phase separation is possible, \( n(T, \tilde{\rho}_g) \) approaches 0 for a range of graft densities. This is because the phase separation interface propagates upwards towards the brush free surface with increasing graft density. Due to this, increasing amount of monomers are packed within the dense region close to the grafting surface and brush height does not change considerably with increasing graft density.

S5 Radius of curvature of a bent substrate

The relation (27) in the main text to calculate the radius of curvature of a bent substrate has been obtained from Manav et al.\(^3\) However, unlike Manav et al.,\(^3\) resultant moment, \( M_s \), has not been ignored. Also, here we ignore Young’s modulus and other material constants for
polymer brush. Thus, \( \tau_s \) and \( M_s \) become independent of the state of bending of the substrate. Notice that (27) is distinct from the classical Stoney equation \((h/R_c = -6\tau_s/(\bar{E}h))\).

For the validity of the plot in Figure 14, three conditions should be satisfied. Firstly, for (27) to be valid, strain should be small, that is \( h/R_c << 1 \). It is satisfied as \( R_c/h > 10 \) in Figure 14. Secondly, a brush should be planar, that is \( H/R_c << 1 \). This is also satisfied since \( H < h \). Finally, strong stretching assumption should hold. Notice that Figure 14 shows results only for graft densities \( > 0.3 \) chains/nm\(^2\). This lower limit on graft density has been set to ensure the validity of strong stretching assumption, which holds only when stretching parameter\(^{4,5} \beta_s = \frac{3}{2} \frac{H^2}{N \tau k_B \sigma} = \frac{3}{2} \frac{N}{\tau_k} \bar{H}^2 \) is larger than a threshold value (taken to be 15 here). For low graft density brushes in a poor solvent, stretching parameter for \( N = 1000 \) is not sufficiently large to ensure validity of this assumption. Utz \textit{et al.}\(^6 \) have argued that at low graft densities when chains in a brush form globules in a poor solvent, lateral stress also originates from surface tension at the globule-solvent and globule-substrate interfaces. This has not been studied in this work.

References


